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A novel method for coating of carbon nanotube on cellulose fiber using 1,2,3,4-butanetetracarboxylic acid as a cross-linking agent

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ABSTRACT

Carbon nanotubes (CNTs) were coated by the exhaustion method and stabilized on a cotton surface using 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent and sodium hypophosphite (SHP) as a catalyst. The Influence of CNTs on the performance of the cellulose fiber was investigated using Fourier transform infrared spectrophotometer (FTIR), thermo-gravimetric analyzer, scanning electron microscope (SEM), zeta potential analyzer, reflectance spectroscope, wrinkle recovery tester and bacteriological culture tube. The possible interactions between CNTs, the cross-linking agent and cellulose functional groups at the surface were elucidated by FTIR spectroscopy. The results indicated that the stabilized CNTs modify the surface of the fibers and increase the thermal stability of the substrate. SEM showed a uniform coating of CNTs on the fiber surface.

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1. Introduction

Carbon nanotubes have unique tubular structures, nanometer diameter and a large length/diameter ratio [1,2]. The basic shape of CNT's wall is a cylinder, which is a graphene sheet rolled into a cylinder of nanometer size diameter [1,2]. CNTs have superior physical and chemical properties and a super strong mechanical performance. Furthermore, they are suitable for many applications such as sensors and probes, thermal resistance, energy storage, optical, electronic and medical applications [2–7]. The excellent mechanical properties of CNTs make them filler material of choice for composite reinforcement therefore CNTs are ideal candidates for reinforcing polymer matrices. In addition, they are known for spinning with various polymers such as poly (lactic acid) [8], bacterial cellulose [9] and polyurethane [10]. However, due to the non-reactive surface of the CNTs, their non-homogenous dispersion and aggregation, they cannot be mixed spontaneously with most polymers [10,11].

Recently a great deal of attention has been focused on applying CNTs on textile fabrics. Various methods have been employed for modifying fabrics using CNTs. Shim et al. produced intelligent e-textiles using a polyelectrolyte-based coating with CNTs [12]. Dyeing fabric with carbon black nano-particles and CNTs has been reported and the exhaustion method has been used for coloration of textiles using surface modified carbon black (self-dispersible carbon black) [13]. Additionally, Panhuis et al. dyed textile material by immersion in either a poly (2-methoxy aniline-5-sulfonic acid) PMAS polymer solution or PMAS-SWNT dispersion with enhanced conductivity and capacitance with a durable behavior [14]. In another study, Hu and coworkers coated single-walled carbon nanotubes (SWNTs) with a simple "dipping and drying" process for wearable electronics and energy storage applications [15]. CNTs have an aligned nanotube structure and a negative surface charge. Therefore, they have similar structures to direct dyes. In this study, for the first time, CNTs were used for coating of cotton fabric at the boiling point by a cationic surfactant as the dispersing agent and an electrolyte to increase absorption and penetration for preparation of the coated fabric. Finally, the after-treatment of fabric with carboxylic acid was carried out to increase the fastness of CNTs. It was observed that carboxylic acid plays a prominent role in stabilizing nanoparticles [16] and CNTs [17]. The direct utilization and stabilization of CNTs in the coating process is considered as a new application of CNTs in textile production. Therefore, this procedure focuses on a novel method for preparing multifunctional fabric.

2. Experimental

2.1. Materials

A desized, scoured and bleached plain weave 100% cotton fabric with 36 wrap/cm and 26 weft/cm was supplied by Yazdbaf

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Fabrics Company (Yazd, Iran). Multiwall carbon nanotubes (MWCNTs) from the Iranian Research Institute of petroleum Industry was used with 5% of carbon impurities. Their length was about 10 μm and the average outer diameter was 10–30 nm. BTCA, SHP, cetyltrimethyl ammonium bromide (CTAB), sodium chloride (NaCl) and Tryptic soy agar (for microbiology) were supplied by Merck Chemical Co., Germany.

2.2. Preparation of colloidal dispersions of MWCNTs and their coating on cotton

Stabilization of MWCNTs on cotton was produced by a three-step method. First, different colloidal dispersions were prepared by mixing 100, 250, 500, 1000 and 1500 ppm MWCNTs, CTAB and deionized water (molar ratio of 1:40). The colloidal dispersions were then treated with an ultrasonic machine at 30 °C for 2 h to reduce the aggregation. Second, the process temperature was initially set at 40 °C and then gradually raised to the boiling point after 20 min. The dyeing baths were then boiled for 25 min and 15 g/L NaCl was gradually added to the dispersions and cotton textiles were dyed through immersion in the prepared baths. The samples were thoroughly rinsed with water, squeezed and dried at the room temperature. Finally, all the samples were dipped in a 50 g/L BTCA with SHP (60% of BTCA) at 40 °C for 20 min and then padded (200% wet pick up) in the prepared solutions. The treated fibers were fully dried at 60 °C in a vacuum and the cross-linking of the fabrics was conducted by curing them at 180 °C for 4 min in a curing oven. The cured fibers were then rinsed with a large amount of deionized water to remove residual MWCNTs, BTCA and SHP for three times.

2.3. Evaluation of samples using Fourier transform infrared spectroscope (FTIR)

The chemical compositions of the fabrics were examined by the FTIR spectroscope [Bruker] in the range of 400–4000 cm^{-1}.

2.4. Thermal properties and flammability

The thermal degradation properties of the samples were performed on a TGA-PL thermoanalyzer from UK. In each case a 5 mg sample was examined under an O_2 at a heating rate of 5 °C/min from room temperature to 650 °C. The flammability of the treated and untreated fabrics was evaluated using a vertical flammability test. A fabric of 15 cm (wrap) × 5 cm (woof) was used. The fabric was exposed to flame for one second and after the ignition the flame was removed. The time for the specimen to burn along with its entire length was recorded [18].

2.5. Evaluation of morphology by microscope

The surface of the fibers was investigated using a Scanning Electron Microscope (SEM) XL30, Philips. The surface of the samples was first coated with a thin layer of gold (10 nm) by Physical Vapor Deposition using a sputter coater (SCDOOS, BAL-TEC).

The cross-section of the coated textile was observed with a Bel photonics polarization microscope (MPL-15) from Italy. Two magnifications were used at 50× and 100× using a CCD camera.

2.6. Determination of zeta potential

The Zeta potential of colloidal dispersion of MWCNTs was measured by a nano-size potential analyzer (Malvern Zetasizer 3000HS).

2.7. Optical assessment

The reflectance of each sample was recorded from 200 nm to 1500 nm using a Cary 500 UV–vis-NIR spectrophotometer (Varian-USA) integrated with an IBM personal computer. The reflectance curves ($R_\infty(\lambda)$) were also converted to the corresponding Kubelka–Munk ratio $(K/S)_\lambda$ of the one constant theory using Eq. (1).

$$\left(\frac{K}{S}\right)_\lambda = \left(\frac{(1-R_\infty(\lambda))^2}{2R_\infty(\lambda)}\right) \quad (1)$$

2.8. Crease resistance, crocking and wash fastness properties

The Crease angle measurements were made by AATCC Standard Test Method 66 using a James Heal Wrinkle Recovery Tester. The results presented here are the recovery angles of the tested fabrics in the warp direction.

Crocking fastness was evaluated according to AATCC Test Method 8 and Assessment was conducted on a gray scale of 1–5 for staining (1–poor, 5–excellent).

The Wash fastness of samples was carried out according to AATCC Test Method 61(2A)-1996 (American Association of Textile Chemists and Colorists, 2000). In this method, one cycle of laundering is considered as equivalent to five home machine launderings at a medium or warm setting at the temperature range of 38 ± 3 °C in the presence of a non-ionic detergent. The color hue changes of the fabrics and the degree of staining on the adjacent fabrics were measured after drying.

2.9. Evaluation of antibacterial efficiency

The antibacterial activity of the treated cotton fabric was tested against two bacteria, *Staphylococcus aureus* (*S. aureus)*, American Type Culture Collection No.6538, as a Gram positive bacterium and *Escherichia coli*, American Type Culture Collection No.11303, as a gram negative bacterium. To this end, some colonies of each bacterium were suspended in a physiologic saline solution (NaCl 0.9% in distilled water at pH 6.5) with concentration of 0.5 Mc Farland. The vials of bacterial suspensions were then incubated with agitation at 37 ± 2 °C, 220 rpm for 2 h. A homogenous suspension of bacteria was prepared and the serial dilution was then done in 5 Steps (dilution of 1:100,000). A concentration of about $1.5–2 \times 10^3$ CFU/ml was applied for the antibacterial testing. The bacteriological culture tubes (i.e., 125 mm × 17 mm glass tubes), containing one piece of the treated cotton fabric (10 mm × 10 mm) were sterilized by an autoclave device in moisturized heat (121 °C, 15 Ib) for 15–20 min. An aliquot of 1 cc bacterial suspension and 2 cc of TSB (Tryptic Soy Broth) was then added to every tube and 3 ml was detected in each tube. To ensure that any decrease in bacterial count was due to the exposure to the cotton fabrics, one control of the saline solution with TSB, and one control of aliquot with the untreated fabrics including the tubes containing the treated cotton fabrics with the bacterial suspensions and the control tubes were incubated at 37 °C for 24 h. The samples of 10 μl from each tube were then taken and counted according to the pour plate method. Thus, the samples were mixed with melted agar (that decreases the temperature down to 45 °C) and poured. The plates incubated at 37 °C for 24 h and the colonies of each plate were counted by a colony counted device to determine the bacteria reduction of the suspensions. The results of the numbers before and after the treatment with the cotton fabrics were used to determine the bactericidal effect and the percentage of reduction of bacteria was calculated using the following equation:

$$\text{Reduction rate}\,(\%) = \frac{100\,(A-B)}{A} \quad (2)$$

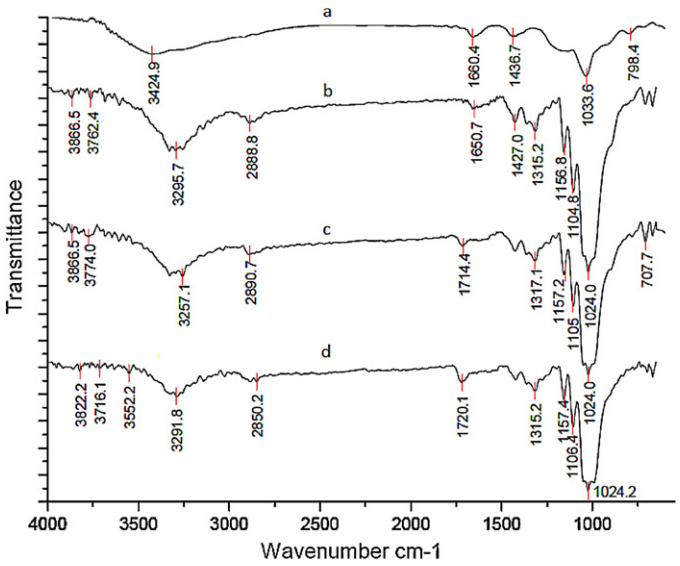

Fig. 1. FTIR spectra of samples: (a) MWCNTs, (b) untreated cotton, (c) cotton cross-linked with BTCA and (d) cotton cross-linked with 500 ppm MWCNTs and BTCA in composite.

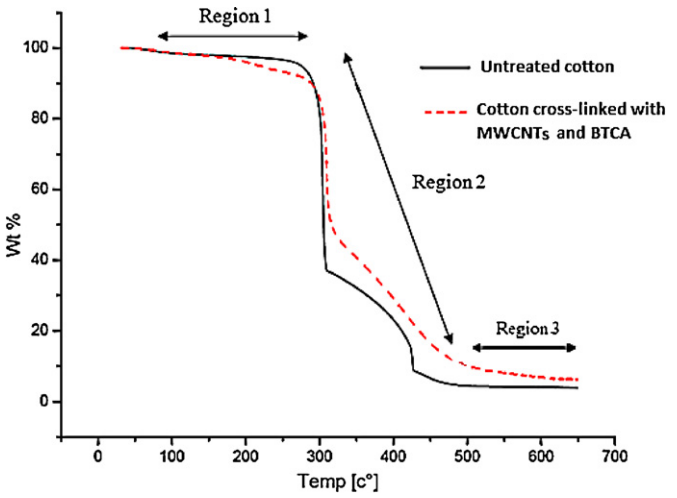

Fig. 2. Thermal degradation of the untreated cotton and sample cross-linked with 1000 ppm MWCNTs and BTCA in composite.

where R is the bacterial reduction ratio, A is the number of bacterial colonies from the untreated fabrics and B is the number of the bacterial colonies from the treated fabrics. All measurements were repeated two times and the standard deviation (the coefficient of variation was below 5% for all cases).

2.10. Mechanical properties and flexural rigidity

The tensile strength and elongation of the untreated cotton and those of the treated one were done by Cesare Gadabini tester according to ASTM D5034 and tear strength according to ASTM D1424. The flexural rigidity tests were carried out according to the BS 3356. This standard describes a method for determination of the flexural rigidity coefficient (G) of the textile. It is related to the quality of stiffness and softness. This coefficient is calculated for wrap directions.

3. Results and discussion

3.1. Structural information by FTIR spectra

The infrared spectra of MWCNTs, the untreated cotton, the cotton cross-linked with BTCA and the cotton cross-linked with the 500 ppm MWCNTs/BTCA composite are shown in Fig. 1.

The incidence of 3424 cm^{-1} width band in Fig. 1a is attributed to the presence of hydroxyl groups (–OH) on the surface of the MWCNTs. The presence of this peak indicates some defects in the MWCNTs crystalline structure even without any pre-treatments. The MWCNTs may react further with the ambient oxygen and the atmospheric moisture to produce oxygenated functional groups during purification of the raw material. Transmittance vibrations at 1033, 1436 and 1660 cm^{-1} can be assigned to C–H deformation and C=C stretching vibration in the aromatic rings [19].

As it can be seen in Fig. 1b, the intense CH_2 asymmetric and symmetric stretchings, O–H stretching and C–H wagging in the plane bending vibrations in cellulose appear at 2888, 3295, 1427 and 1315 cm^{-1}, respectively. The bands appearing at 1650 and 1024 cm^{-1} represent bending and stretching motions of the adsorbed water molecules and C–O bonds in the cotton chains. The Etheric bonds for cotton were characterized by strong C–O–C symmetric and asymmetric stretching vibrations at 1104 and 1156 cm^{-1} [20,21].

After cross-linking of the cotton with BTCA and MWCNTs/BTCA composite (Fig. 1c and d), a small band at 1650 cm^{-1} disappeared and the two bands appearing at 1714 and 1720 cm^{-1} can be characterized as ester and carboxylate carbonyl in the cross-linked cellulose. This could be due to a decrease in the total number of hydroxyl and carbonyl groups of cellulose through the cross-link formation between the cotton and the MWCNTs/BTCA composite [20,21].

3.2. Determination of thermal properties

Fig. 2 summarizes the thermal degradation of the untreated cotton and that of the cotton cross-linked with MWCNTs and BTCA. As it can be seen from the figure, the TGA curves of the cotton consist of three regions of 1, 2 and 3 as initial, main, and char decomposition regions. In the first stage, the changes of the thermal properties and the weight loss of fibers are due to some physical damages occurring mostly in the amorphous region of the cellulose. The main thermal stage occurs in the second region, where the weight loss is significant. It is stated by different researchers that glucose together with all kinds of combustible gases are generated in this region [22]. They found that thermal degradation in this region takes place in the crystalline region of cellulose fibers. The production of char occurs at the third region at higher temperatures of 400 °C. This process continues by dewatering and charring reactions, releasing water and carbon dioxide and increasing the carbon and charred residues [23]. The sample cross-linked with MWCNTs and BTCA showed a higher degradation at the second region. This improvement of thermal properties is attributed to the high heat resistance, the heat insulation effect and the mass transport barrier toward cellulose molecular chains exerted by the MWCNTs themselves, which are a measure of flame retardancy. On the other hand, the interaction between the cotton surface, MWCNTs and BTCA was fairly strong which effectively restricted the motions of the molecular segment in cellulose. This is also consistent with our results obtained from FTIR spectra [24]. Table 1 shows Burning time/s for the untreated cotton and those cross-linked with different amounts of MWCNTs and BTCA in composite. As a result, the fabrics show improved flame retardency when they are exposed to flame. Untreated cotton ignited easily due to its tendency to flame. However from Table 1 it is clear that the burning behavior for the sample treated with 100 ppm MWCNT was decreased

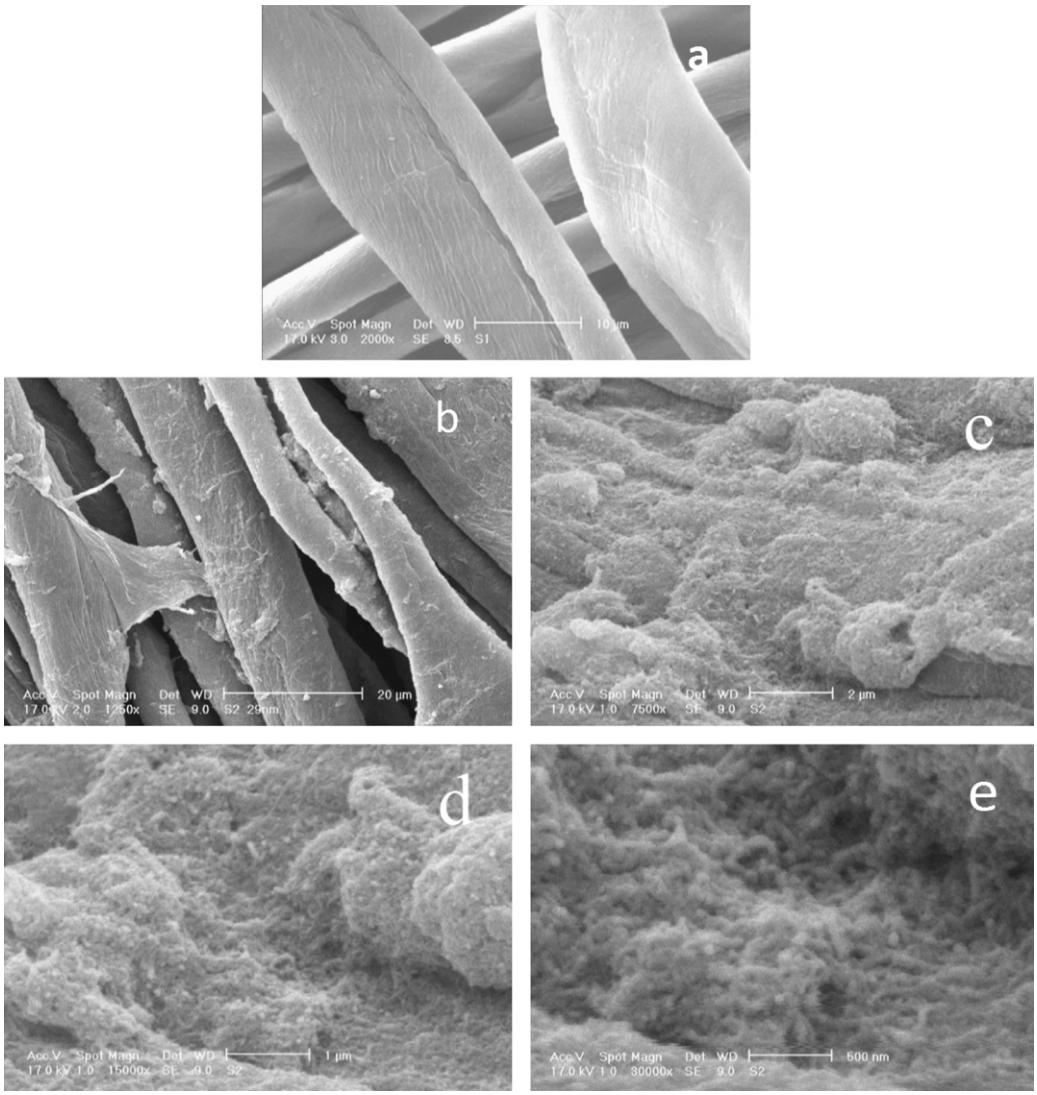

Fig. 3. SEM images of (a) the untreated cotton fiber at 2000×. (b) The cotton fiber cross-linked with 500 ppm MWCNTs and BTCA in the composite at 1250×. (c) The cotton fiber cross-linked with 500 ppm MWCNTs and BTCA in the composite at 7500×. (d) The cotton fiber cross-linked with 500 ppm MWCNTs and BTCA in the composite at 15,000×. (e) The cotton fiber cross-linked with 500 ppm MWCNTs and BTCA in the composite at 30,000×.

and the flame speed was slower than that of the untreated fabric. An increase in MWCNT concentration caused a greater decrease in flammability. Cotton is a semi-crystalline polymer whose thermal properties and flammability are influenced by its molecular structure, density, crystallization level, crystal orientation angle and mobility of the molecular chains in amorphous and crystalline regions. Researchers have claimed that the flame-retardant effect found in the polymer–CNT composites arises from the formation of the char layers, which are due to the uniform dispersion of CNTs within the composites. Others have stated that the some nanoparticles such as MWCNTs in the composite act as radical scavengers to delay the thermal degradation and thus improve the thermal stability [25,26].

Table 1
Crease recovery angles and burning time for the untreated cotton together with those cross-linked with BTCA and various MWCNT content in the composite.

MWCNT content (ppm)	Recovery angle (°)	Burning time/s
–	93.40	16.6
100	118.2	17.9
250	124.8	21.2
500	129.2	23.6
1000	140.4	29.5
1500	145.6	30.1

3.3. Microscopic characterization

The SEM images of the untreated cotton fiber and the sample cross-linked with 500 ppm MWCNTs and BTCA in the composite are shown in Fig. 3a–e. It can be seen that the untreated fiber has grooves and fibrils with a relatively smooth surface. The surface of the untreated fiber has no deposition of MWCNTs and a cross-linking agent. The high magnification SEM images of the cotton fiber cross-linked with MWCNTs and BTCA show a formation of few aggregated CNTs on the surface of the cotton. It is evident that the MWCNTs-BTCA composite was relatively well dispersed on the surface of the fiber with a thin layer of CNTs coating.

In general, the ability of nano-particles to aggregate on the surface of textiles and polymers is defined by several factors such as size, mobility, end-group functionalities, relative composition and molecular architecture [25–27]. As mentioned previously, the FTIR spectra of samples illustrate that carbonyl and hydroxyl groups of cotton cross-link with carboxylic groups of BTCA. It seems that these interactions are strong enough to allow the deposition of

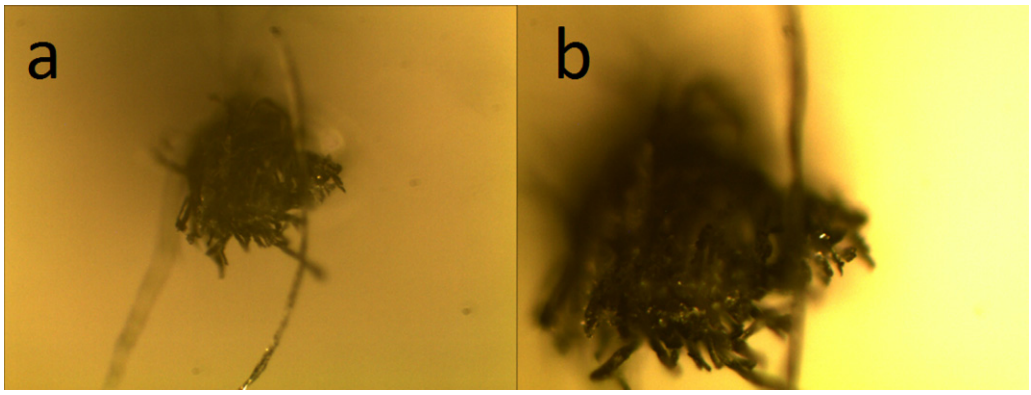

Fig. 4. Cross section of the cotton fibers cross-linked with 1000 ppm MWCNTs and BTCA in the composite: (a) 50× and (b) 100×.

MWCNTs on the cellulose surface as a result of their high surface area.

It has been shown by several researchers that the unique properties of CNTs can be attributed to their small dimensions, or to their large aspect ratios. Our findings showed that the significant surface area of CNTs promotes sufficient interactions and aggregation on the textile. This depends on how chemical bonds between the CNTs, BTCA and cotton can enhance the coating process. Intrinsic van der Waals attraction among tubes in combination with their high surface area and high aspect ratio often leads to significant aggregation; hence promoting efficient transfer of their superior properties to the nanocomposite coating [2–7]. Other authors have confirmed this phenomenon in cases where nano-particles were incorporated into multilayer organic coatings [28,29].

The images of cross-sections for cotton fibers cross-linked with 1000 ppm MWCNTs and BTCA in the composite at two magnifications of 50× and 100× are shown in Fig. 4. The MWCNTs are homogeneously adsorbed on the cotton surface.

3.4. Determination of zeta potential

Pristine CNT is extremely hydrophobic and prone to aggregate and deposit in water due to the high van der Waals interaction forces along the length axis. The hydrophobic nature leads to a poor dispersion of MWCNTs into a uniform and stable suspension. In order to achieve this purpose, we applied a non-covalent functionalization method for the preparation of the stable aqueous suspensions of MWCNTs. It was found that this method drastically improves the stability of the CNT suspensions without any changes in the properties of CNTs [30,31].

Fig. 5 proves the increased stability of the MWCNTs against aggregation with no signs of coagulation of the MWCNTs after one month. It was found that the absorption of CTAB on the surface of CNTs greatly changed zeta potential of the MWCNTs from being negative (−32.6 mv) to positive (46.3 mv). According to ASTM Standard (D 4187-82), colloids with zeta potential from ±30 to ±40 has a moderate stability while having a good stability with zeta potential of ±40 to ±60 [32]. A CTAB surfactant can disperse CNTs in water by sonication preventing its precipitation and aggregation. The surfactant may be adsorbed onto the CNT surfaces through hydrophobic attraction with its hydrophobic tails binding to the CNT surface and hydrophilic head groups extending towards the solution [33]. The adsorption of CTAB could transfer a positive charge to the CNT surfaces rendering zeta potential of the CTAB-stabilized CNTs more positive than the pristine CNT in water. Some researchers have claimed that the driving force for the adsorption of ionic surfactants onto the charged surfaces could be the Coulombic attractions, which were formed, for example, between the surfactant's positively-charged head group and the negatively-charged solid surface. However, the original negative charge on the pristine CNT surface could be neutralized by the positively-charged head group of CTAB, and the excessive CTAB may mainly get adsorbed onto the CNT surface [32,33].

3.5. Reflectance assessment

The surfactant used in this study significantly increased the dispersability of the MWCNTs in water. The aim was to apply the MWCNTs to dye cotton fibers as cationic dyes in the presence of an electrolyte. In water, cellulose carries negative charges, which together with the positive charges of the dispersed MWCNTs cause an electrostatic attraction. Through addition of NaCl to the bath and increasing the temperature of the process, this electrostatic repulsion is postponed, which causes a better interplay of electrostatic and van der Waals forces leading to a greater affinity to cotton [34]. To improve the performance of MWCNTs on cotton, BTCA was used in the presence of SHP as a catalyst. BTCA is an environmental friendly cross-linking agent of cotton used for the crease resistance finishing. Cotton cellulose is esterificated with BTCA by intermediate formation of a five member cyclic anhydride of two carboxyl groups. Intermediate cyclic anhydride can subsequently react with the cellulose hydroxyl, forming a covalent bond to complete the ester linkage [20,21,35]. In a further reaction, other carboxylic anions of BTCA can react with dispersed MWCNTs through formation of electrostatic interactions. Fig. 6 shows the mechanism of adsorption of MWCNTs on cellulose followed by stabilization in a reaction with BTCA. The influence of the added salt is the most important factor in the coating of cellulose fiber with MWCNTs.

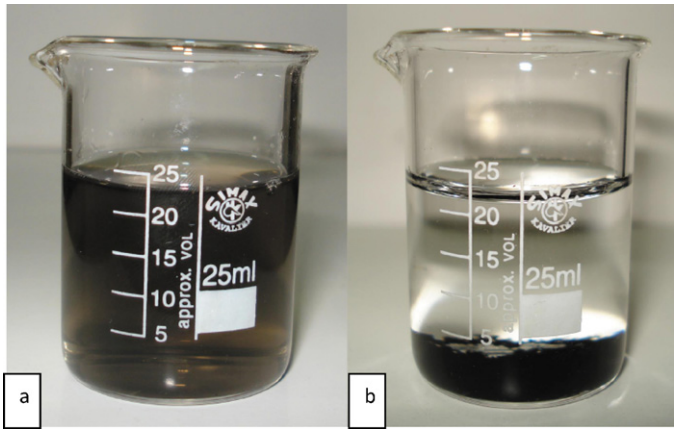

Figure 5. Stability of the MWCNTs in water after one month. (a) After treatment with CTAB and (b) before treatment with CTAB.

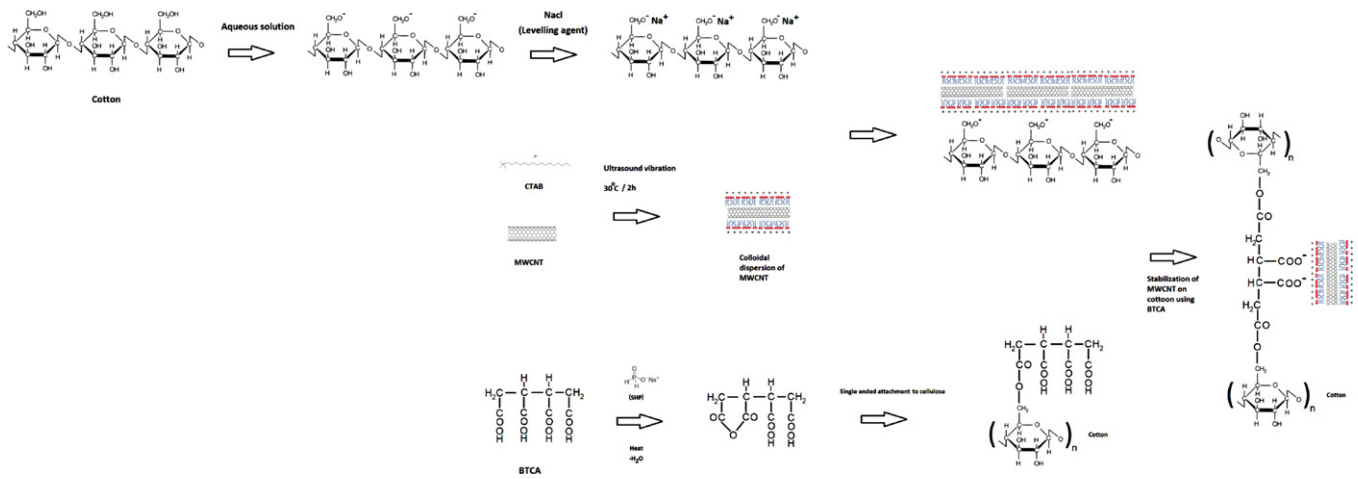

Fig. 6. The mechanism of adsorption of MWCNTs on cellulose and its stabilization in the reaction of BTCA with cellulose.

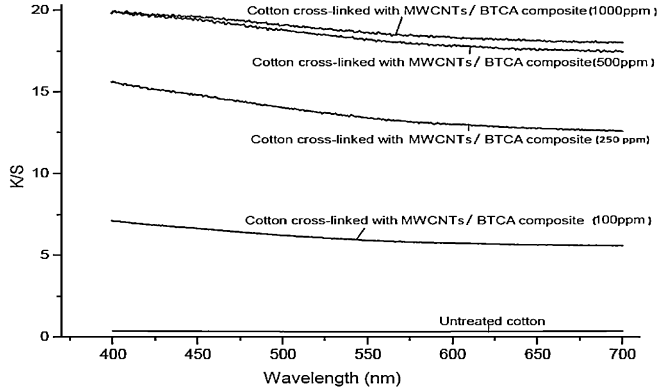

Fig. 7. K/S values of the cotton fabrics cross-linked with different concentrations of MWCNTs in MWCNTs/BTCA composite.

The salt provides sodium ions to counteract the negative surface charge of wet cotton and high temperature ensures good leveling and better penetration of the MWCNTs into the fibers. There are two objectives for coating of cellulose fiber with MWCNTs: good exhaustion and good uniformity. This mechanism can be demonstrated by K/S values of the MWCNTs stabilized cotton fabrics in the considered visible region as illustrated in Fig. 7. The K/S values increased after the treatment of the cotton with the MWCNT/BTCA composite (100 ppm MWCNTs in dispersion). Apparently, increasing the MWCNT concentration in baths increased the K/S values. Based on the results, there was not a considerable increase in K/S values of the cotton treated with 1000 ppm MWCNTs as compared with that treated with 500 ppm. Fig. 8 shows the pictures of the untreated cotton with that cross-linked with the 1000 ppm MWCNTs/BTCA composite.

To study the reflectance spectra of the cotton cross-linked with various MWCNTs/BTCA composites in comparison with that of the untreated cotton at wavelengths lower than 900 or higher than 950 nm, reflectance spectrophotometer was also elucidated and the results are summarized in Figs. 9 and 10. As it is evident in both figures, the reflectance values for the cotton cross-linked with the 100 ppm MWCNTs/BTCA composite decreased in the considered spectral regions followed by a bigger decrease as the MWCNT concentration increased in the composite. The decrement of reflectance values at the visible region for the coated fibers could possibly be due to the π-band's optical transitions of the CNTs, their extremely low refractive index and trapping of light in the composite coating after multiple reflections [36]. Some researchers have used vertically aligned single-walled CNTs for the preparation of a black body absorber. They found that the optical behavior of the CNTs originates from their homogeneous sparseness and alignment. The aligned nanotube arrays can be birefringent and strongly absorb the visible light [37].

Our study also demonstrated a decrease in reflectance values at the infrared region for the samples coated with MWCNTs/BTCA composites. CNTs have a tunable infrared absorption that makes

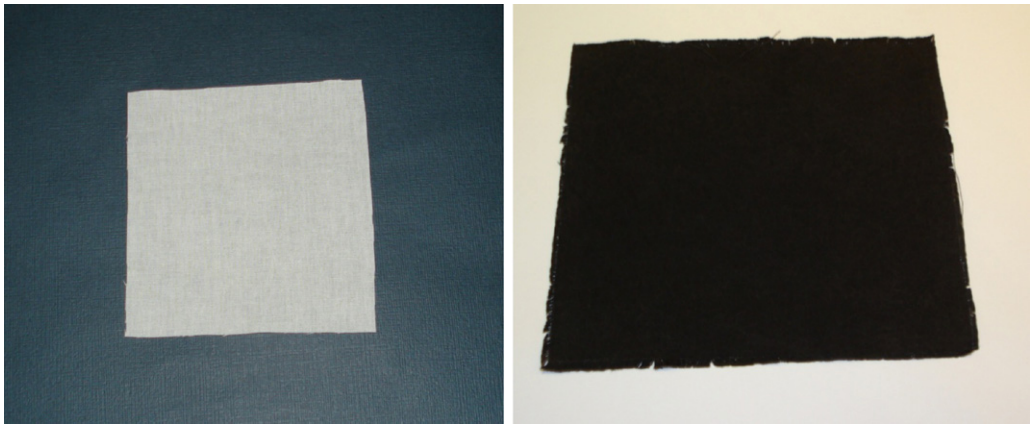

Fig. 8. Cotton fabric before and after cross-linking with 1000 ppm MWCNTs/BTCA composite.

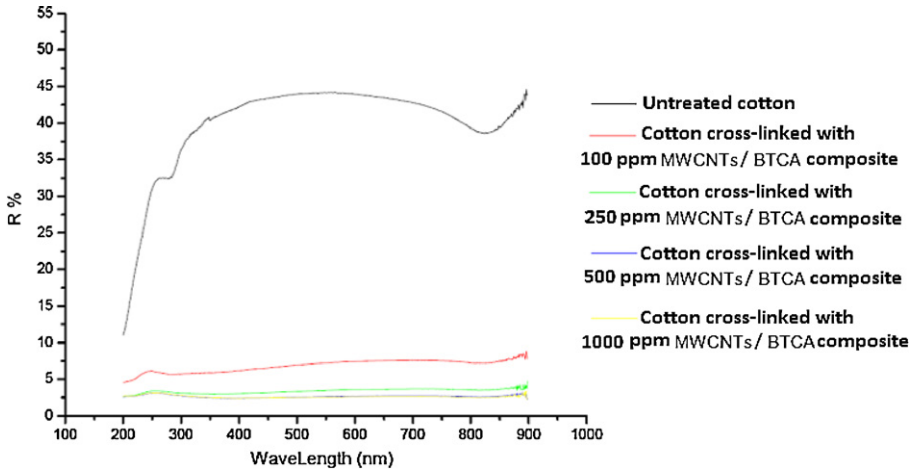
R %
WaveLength (nm)
Untreated cotton
Cotton cross-linked with 100 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 250 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 500 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 1000 ppm MWCNTs/ BTCA composite

Fig. 9. Reflectance of the cotton fabrics cross-linked with different concentrations of MWCNTs in MWCNTs/BTCA composite at wavelengths lower than 900 nm.

Table 2
Wash fastness for the untreated cotton in the presence and absence of BTCA and various MWCNT content in the composite.

MWCNT content (ppm)	Wash fastness (without crosslinking)	Wash fastness (with crosslinking)	Staining on wool (with crosslinking)	Staining on cotton (with crosslinking)
100	5	5	5	5
250	4/5	5	5	5
500	4/5	5	5	5
1000	4/5	5	5	5
1500	4/5	5	5	5

them an attractive candidate for applications ranging from solar energy conversion to pyroelectric detectors and infrared devices [38,39].

3.6. Crease resistance, crocking and wash fastness properties

The crease recovery angles and wash fastness measured for the treated fabrics are given in Table 1. As it can be seen, the recovery angle increased for the sample cross-linked with BTCA and more increase was observed with the addition of MWCNTs in the dispersion. An increase in MWCNT content in the composite caused more increment in the wrinkle recovery angle value.

After cross-linking of the cotton with BTCA, the hydroxyl groups of cellulose chains included cross-linking by ester linkages in the less-oriented (paracrystalline) or amorphous regions of cellulose. Thus, it improved the crease recovery of the textile. CNTs generate a three dimensional network on the cotton through formation of electrostatic interactions with these cross-linked BTCA chains, which improves the crease resistance of the fabrics [35].

For the wash-fastness tests of the colored cotton samples, a piece of dyed textile was sewn together with white pieces of wool and cotton clothes and washed according to a standard procedure. The discoloration of the white pieces of the textile or, in other words, the bleeding properties of the MWCNTs was recorded. Bleeding is the transfer of MWCNTs to a secondary, accompanying fiber material during washing. As for most general properties of dyes, five classes can be mentioned for characterizing the wash fastness: grey scale or class 1 which is very poor; class 2, poor; class 3, fair; class 4, good; and class 5, excellent. All the composite coated samples indicated excellent wash fastness on the cotton (Table 2). On the other hand, the wash fastness is decreased for the treated fabric without BTCA [40–43]. Additionally, in Table 3, the coated fabrics possess very good crocking fastness in low concentrations of 100 and 250 ppm in wet and dry conditions. It can be seen that fastness was decreased

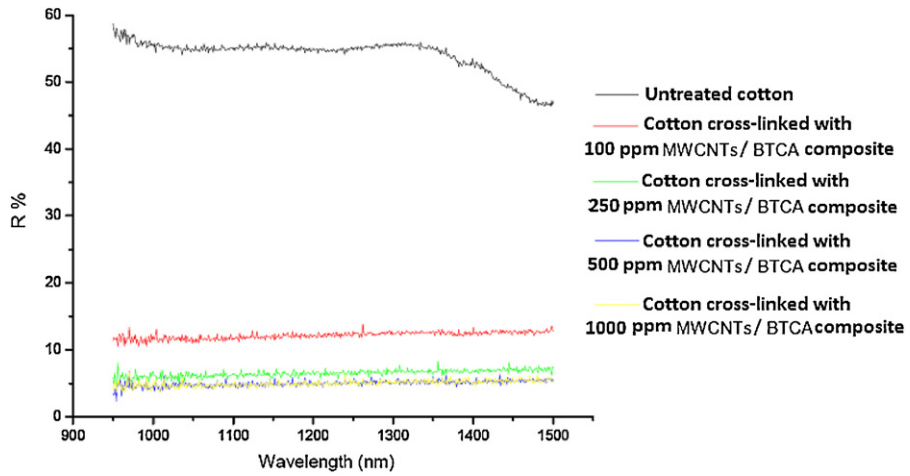
R %
Wavelength (nm)
Untreated cotton
Cotton cross-linked with 100 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 250 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 500 ppm MWCNTs/ BTCA composite
Cotton cross-linked with 1000 ppm MWCNTs/ BTCA composite

Fig. 10. Reflectance of the cotton fabrics cross-linked with different concentrations of MWCNTs in MWCNTs/BTCA composite at wavelengths higher than 950 nm.

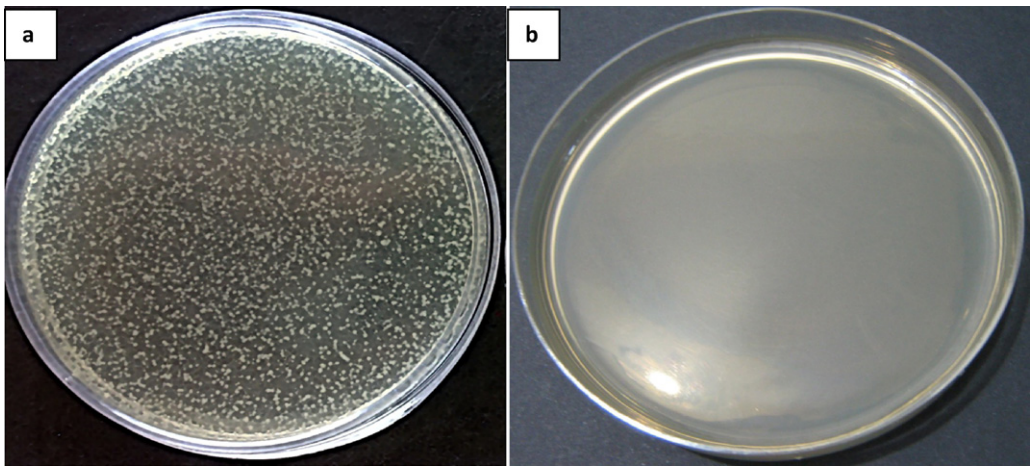

Fig. 11. The colonies of *S. aureus* corresponding different samples: (a) untreated cotton and (b) sample treated with MWCNTs/BTCA composite (100 ppm).

Table 3
Crocking fastness for the untreated cotton with those cross-linked with BTCA and various MWCNT content in the composite.

MWCNT content (ppm)	Dry crocking	Wet crocking
100	5	5
250	5	4/5
500	5	4/5
1000	4/5	4
1500	4/5	4

after increasing nanotubes content but they showed good crocking fastness. This result indicates good penetration of the nanotube into the cellulose fiber.

BTCA improves wash fastness through cross-linking reactions. An improvement in the fastness properties occurs during the reaction of dispersed MWCNTs with one molecule of BTCA through the formation of an ester bridge [20,21,35]. It is also possible that one BTCA molecule could react with MWCNTs and two hydroxyl groups of cellulose. The interaction between the MWCNTs and the BTCA is mainly the ionic attraction from the positively charged nitrogen of surfactant on MWCNTs and the negatively charged BTCA molecules. In other words, due to a charge in neutralizing mechanism, the negative charges of cross-linking agent could efficiently neutralize the positive charges on MWCNTs and decrease their solubility. On the other hand, it was confirmed that through adding BTCA as a cross-linking agent and SHP as a catalyst, BTCA crosslinked with cellulose by covalent bonds and CNTs entrapped physically on the cellulose structure. Cross-linking agent might be embedded the nanotubes more firmly in compare the fabric without cross-linking agent [16,44].

3.7. Evaluation of antibacterial properties

The antibacterial effect of MWCNTs requires a direct contact between MWCNTs and microorganisms. Fig. 11 depicts the colonies of *S. aureus* corresponding the untreated cotton and the sample treated with MWCNTs/BTCA composite (100 ppm). The results showed that MWCNTs have a positive effect on antibacterial properties of the coated textile samples. The reduction rates for both Gram-positive and Gram-negative bacteria were 99.9% by the CNT embedded textiles even for the fabric with 20 ppm concentration.

The previous studies have showed that CNTs add an adhesive ability to microorganisms. They can be used in the removal of a diverse range of biological contaminants including bacteria, viruses, natural organic matters and cyanobacterial toxins. This is due to their fibrous shapes which impinge the bacterial cell surface, disrupting the intracellular metabolic pathways. Subsequently, the internal contents are released due to the cell rupture caused by the oxidative stress [45,46].

3.8. Mechanical properties

Table 4 shows that the strength of the treated fabrics is decreased after the cross-linking process. An increase in CNTs further decreases the strength of the treated fabrics. The decrement of tensile and tear strength of the cotton treated may be due to two different factors: first, irreversible acid-catalyzed depolymerization and reversible crosslinking of cellulose molecules with BTCA may cause a decrease in strength. Second factor could be the result of hydrolytic action of BTCA on the cotton chains and restriction of stress distribution within the cross-linked fiber [47–51]. Additionally, there is not an effective reaction between CNTs and cellulose and there are physical van der Waals and anionic linkages so any increase in CNTs concentration has no

Table 4
Tensile strength, tear strength, elongation and flexural rigidity for the untreated cotton with those cross-linked with BTCA and various MWCNT content in the composite.

MWCNT content (ppm)	Tensile strength (N/mm^2)	Elongation (%)	Tear strength $N \times 10^{-3}$	Flexural rigidity (mg cm)
Untreated cotton	34.5	14.9	659.7	17.3
100	28.2	37.9	453.3	47.6
250	25.0	34.1	430.2	60.9
500	22.9	32.5	402.6	65.8
1000	15.6	21.8	380.0	94.6
1500	14.8	20.3	352.1	95.1

positive effect on mechanical properties of the fabric. On the other hand, through increasing the concentration of CNTs, nanotubes set among molecular chains of cross-linking agent and cross-linked contraction are decreased. Therefore, increasing the concentration of CNTs decreased the strength of cotton. It is also observed that the flexural rigidity increases as the amount of CNTs increases. This means that those fabrics became slightly stiffer and less flexible as a result of the treatment [18].

4. Conclusion

MWCNTs and a cross-linking agent were used to fabricate a multifunctional coating on the cotton through an exhaustion then pad-dry-cure after-treatment method. The stabilization of CNTs in the composite coating was achieved by a reaction of BTCA and cellulose chains. This reaction process resulted in the attachment of MWCNTs to the surfaces of the cellulose fibers. The FTIR spectra showed the cross-linking reaction between the carboxylic acid group of BTCA and cellulose to form ester and ether groups in the presence of CNTs under curing. The results obtained from the tests demonstrated an improvement of the thermal properties and flammability of the coated samples. This can be as a result of a high heat resistance, a heat insulation effect and the mass transport barrier of CNTs embedded in the coating. Zeta potential analysis confirmed a successful dispersion of MWCNTs in the aqueous suspension using a non-covalent surfactant. Moreover, MWCNTs stabilized in the coating decreased the reflectance values at the visible region, which can be attributed to the low refractive index and high absorbance properties of the coating.

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